

Process for making multilayer coatings using a radially or cationically polymerisable clear coat.

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Abstract

A process for making a multilayer coating by applying a clear coat varnish exclusively comprising coating compositions which can be cured by means of free-radical and/or cationic polymerisation to a dried or crosslinked, colour-providing and/or effect-providing base coat, under illumination with light having a wavelength of greater than 550 nm or in the absence of light, and subsequently initiating or carrying out the curing of the clear coat by means of high-energy radiation. The process is particularly suitable for making multilayer coatings in the automotive sector.

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(54) PROCESS FOR PRODUCING MULTI-LAYER LACQUER COATINGS BY THE USE OF CLEARLACQUERS WHICH ARE CAPABLE OF POLYMERISATION IN RADICALIC AND/OR CATIONIC MANNER

(54) PROCEDE DE LAQUAGE MULTICOUCHE METTANT EN OEUVRE DES LAQUES CLAIRES POLYMERISABLES PAR VOIE RADICALAIRE ET/OU CATIONIQUE

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ABSTRACT:

Herberts GmbH

Process for producing multi-layer lacquer coatings by the use of clear lacquers capable of being polymerized in radicalic and/or cationic manner

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Process for producing a multi-layer lacquer coating by the application of a coat of clear lacquer consisting of coating agents which are curable exclusively by polymerisation in radicalic and/or cationic manner to a dried or crosslinked coloured and/or effect-producing basecoat film, the process taking place in light having a wavelength of over 550 nm or subject to the exclusion of light, this being followed by initiation or implementation of curing of the clear-lacquer film by high-energy radiation. The process is particularly suitable for producing multi-layer lacquer coatings in the automobile industry. 22

CLAIMS: [Show all claims](#)

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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for Producing Multi-Layer Lacquer Coatings by
the Use of Clear Lacquers Which are Capable of
Polymerisation in Radicalic and/or Cationic Manner

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Herberts GmbH

Process for producing multi-layer lacquer coatings by the use of clear lacquers capable of being polymerised in radicalic and/or cationic manner

ABSTRACT

Process for producing a multi-layer lacquer coating by the application of a coat of clear lacquer consisting of coating agents which are curable exclusively by polymerisation in radicalic and/or cationic manner to a dried or crosslinked coloured and/or effect-producing basecoat film, the process taking place in light having a wavelength of over 550 nm or subject to the exclusion of light, this being followed by initiation or implementation of curing of the clear-lacquer film by high-energy radiation. The process is particularly suitable for producing multi-layer lacquer coatings in the automobile industry.

CLAIMS

1. Process for producing a multi-layer lacquer coating by the application of a clear lacquer coating to a dried or crosslinked basecoat film which is coloured and/or has a special finish, characterised in that in order to produce the clear-lacquer coating a coating agent is used which is curable exclusively by radicalic and/or cationic polymerisation, application of the coating agent being effected subject to illumination with light having a wavelength of over 550 nm or subject to the exclusion of light, whereupon curing is initiated and/or implemented by high-energy radiation.
2. Process according to Claim 1, characterised in that curing is initiated and/or implemented with UV radiation in the wavelength range from 180 to 420 nm.
3. Process according to any of the preceding Claims, characterised in that curing is initiated and/or implemented by irradiation with electron rays.
4. Process according to any of the preceding Claims, characterised in that curing is effected by two or several high-energy sources of radiation in succession in two or more stages.
5. Process according to any of the preceding Claims, characterised in that after initial curing by high-energy radiation curing is additionally effected by thermal means or is continued by thermal means.

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6. Process according to Claim 5, characterised in that it is carried out with a coating agent curable by radicalic polymerisation and which contains one or several photoinitiators and one or several radical initiators which are capable of being activated thermally.
 7. Process according to Claim 5, characterised in that it is carried out with a coating agent curable by cationic polymerisation and which contains one or several photoinitiators.
 8. Process according to any of the preceding Claims, characterised in that it is carried out with a coating agent containing transparent pigments and/or soluble dyestuffs.
 9. Process according to any of the preceding Claims, characterised in that a coating agent is used which is essentially free from solvents or contains water as solvent.
 10. Process according to any of the preceding Claims, characterised in that the clear lacquer coating is applied with a dry layer thickness of 10 - 80 μm .
 11. Process according to any of the preceding Claims, characterised in that the coating agent is applied by spray and overspray accruing is optionally recycled for spray application after replacement of volatile components.
 12. Use of transparent coating agents as clear lacquers in producing multi-layer lacquer coatings which are curable by radicalic and/or cationic polymerisation and optionally contain transparent pigments and/or soluble dyestuffs.

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13. Use according to Claim 12 in the production of multi-layer lacquer coatings in the automobile industry.

Process for producing multi-layer lacquer coatings by the use of clear lacquers which are capable of polymerisation in radicalic and/or cationic manner

The invention relates to a process for producing a multi-layer lacquer coating with a mechanically stable quick-drying clear-lacquer coating based on systems curable by radiation.

Coatings as applied in the series production of automobiles nowadays mostly consist of a surface lacquer of basecoat and clear lacquer which is applied to bodywork that has been electrophoretically primed and coated with filler. In this process basecoat and clear lacquer are preferably applied wet-on-wet, i.e. after a flash-off period optionally subject to heating and after subsequent application of a clear lacquer the basecoat is stoved together with this lacquer, as described for example in EP-A-38 127 and EP-A-402 772. In this connection suitable clear lacquers are described, for example, in EP-A-38 127 and EP-A-184 761. The stoving process in industrial production lacquering requires long drying phases, and naturally a certain time passes before the lacquer is no longer tacky, so that special measures have to be taken in order to avoid incorporating dust in the surface.

Both in the case of the use of one-component (1C) and also of two-component (2C) clear lacquers the lacquering process is associated with emissions of environmentally harmful solvents or dissociation products of the crosslinking reaction. In the case for example of isocyanate-crosslinking 2C clear lacquers, e.g. according to DE-OS 33 22 037 or DE-PS 36 00 425, recycling of overspray is by its nature not possible.

In JP-A-6213 2570 clear UV lacquers are described which serve to protect electrical instruments used in domestic appliances and in the automobile industry. They are applied in a thin film; multiple precoating does not take place.

In EP-A-0 118 and GB-A-2 226 566 UV-curable layers are described for protecting automobile underbodies from the impact of stones. The layers are applied with a thickness of up to 1500 μm . They are formulated so as to be soft and elastic and are not capable of being ground.

In EP-A-0 247 563 coatings are described which by way of surface lacquer have a coating which in addition to an isocyanate-hydroxyl-group crosslinking reaction is also subjected to crosslinking by UV radiation. The overspray accruing during application of the coating agent can in view of the chemical reaction no longer be subjected to recycling.

The object of the invention is to make available a lacquering process for a multi-layer lacquer coating, in particular for the automobile industry, in which a clear lacquer enabling fast crosslinking is used as surface-lacquer coating, in which process the overspray following application can be recycled, and in which a shiny or matt, hard and clear surface lacquer is produced by way of substrate coating.

It has been shown that this aim can be achieved by a process for producing a multi-layer lacquer coating in which a liquid clear lacquer which can be crosslinked exclusively by radicalic and/or cationic polymerisation is applied to a previously dried basecoat layer. Application of the clear lacquer is effected while daylight is screened off, optionally during illumination with visible light having a wavelength of over 550 nm. The overspray accruing during application of the clear lacquer is collected and can optionally be re-used for spraying after recycling. Curing of the clear-lacquer layer is subsequently effected by irradiation with high-energy radiation or is initiated by irradiation with high-energy radiation.

An advantage of the process according to the invention consists in the fact that substrates which are sensitive to

temperature can also be provided with a durable layer of surface lacquer. In addition, as a result of short reaction and drying times, pollution of the freshly lacquered surface can be avoided. The surfaces obtained in this way have good optical characteristics and a high degree of resistance to scratching.

> The lacquer systems which can be used according to the invention all make use of coating agents which are curable by radiation and which crosslink exclusively as a result of radicalic or cationic polymerisation or combinations thereof. Aqueous systems rich in solids and occurring as emulsions constitute a preferred embodiment of the invention. But coating agents containing solvents can also be used. Particularly preferred are 100% lacquer systems which can be applied without solvent and without water. The clear lacquers curable by radiation can be formulated as unpigmented or transparently pigmented surface lacquers, optionally coloured with soluble dyestuffs.

The clear-lacquer coatings can be applied to conventional basecoats. These may contain solvents or be of an aqueous or powdery type. The basecoats contain conventional physically drying and/or chemically crosslinking binding agents, inorganic and/or organic colouring pigments and/or pigments producing special effects, such as metallic pigments or those giving a pearly-lustre, as well as other auxiliary substances which are customary in lacquering, such as catalysts, levelling agents or anti-cratering agents. These basecoats are applied to conventional substrates either direct or on pre-coated substrates. Prior to application of the basecoat the substrates can, for example, be provided with conventional primer, filler and intermediate layers such as are customary for, e.g., multi-layer lacquer coatings in the automobile industry. Metal or plastic parts are suitable as substrates.

Prior to coating with radiation-curable lacquers the layers of primer are dried or stoved under such conditions as to ensure that they only contain small amounts of volatile substances. In particular, at the time of the radiation-induced crosslinking reaction of the layer of clear-lacquer coating no substantial amounts of volatile components should any longer be present in the basecoat layer. Such components can impair gloss and adhesion in the clear-lacquer film. Drying of the basecoat layer can be effected at room temperature or at temperatures up to 150°C. This does not exclude the possibility of a chemical crosslinking reaction.

In the particularly preferred case of solvent-free radiation-curable clear-lacquer systems, the process according to the invention enables a particularly good metal effect to be achieved on metallic basecoats by way of basecoat layer.

After application and drying of the basecoat the workpiece is provided with the radiation-curable surface lacquer. Until the workpiece is discharged from the coating unit the coating process is carried out subject to illumination with visible light having a wavelength of over 550 nm or subject to the exclusion of light. To this end necessary measures for screening off other light sources are optionally employed, e.g. light traps at the entrances and exits of the lacquering plant, filters in front of light sources or measures for preventing reflection. Only light sources are used that have an emission spectrum starting at above 550 nm. Such sources are, e.g., lamps provided with UV filters or yellow filters. Illumination can optionally also be effected from outside by the use of windows. During stages of the process which run automatically and need no optical control it is of course possible to proceed subject to the exclusion of light, so that the above-stated light sources only have to be switched on if a fault occurs. In the case of pure electron-ray

curing with suitable lacquer systems work can also proceed under normal lighting conditions.

Application of the radiation-curable lacquer can be carried out by all conventional spray-application methods, such as, e.g., compressed-air spraying, airless spraying, high-speed rotation, electrostatic spray application (ESTA), optionally coupled with hot-spray application such as hot-air spraying, at temperatures not exceeding 70 - 80°C, so that suitable application viscosities are achieved and no change in the lacquer material or the overspray to be recycled occurs during the short time that the thermal treatment is applied. In this way hot spraying can be organised in such a way that the lacquer material is only heated for a short time in the spray jet or a short distance upstream of it.

The spraying booth may optionally be a circulation-type booth of adjustable temperature, operated with an absorption medium suitable for the overspray, e.g. the lacquer material. The spraying booth consists of materials which exclude the possibility of contamination of the material to be recycled and which are not affected by the circulating medium. Examples are high-grade steel or suitable plastics.

By avoiding light with a wavelength below 550 nm the lacquer material used and the overspray are not affected. This enables direct reprocessing. The recycling unit essentially comprises a filtration unit and a mixing device which maintains an adjustable ratio of fresh lacquer material to be reprocessed and optionally circulating lacquer material. In addition, storage containers and pumps as well as control devices are present. With the use of non-100% lacquer material a mixing device is necessary for keeping a constant level of volatile components such as organic solvent components or water.

Application is performed in such a manner that dry layer

thicknesses of preferably 10 - 80 μm , and in particular 30 - 60 μm , are achieved. Application of the clear lacquer can optionally be effected in several layers.

After application of the clear-lacquer coating agent the coated substrate is optionally subjected after a rest period to the crosslinking process. The rest period serves for example to enable levelling, degassing of the lacquer film or evaporation of volatile components such as solvents, water or CO_2 if the lacquer material has been applied using supercritical carbon dioxide as solvent, as described for example in EP-A-321 607. It can optionally also be supported by increased temperatures of up to 80°C , and preferably up to 60°C .

The actual radiation-curing process can be carried out either by UV radiation or electron-ray radiation or with actinic radiation emitted from other radiation sources. In the case of electron-ray radiation it is preferable to work in an atmosphere of inert gas. This can be achieved for example by supplying CO_2 , N_2 or a mixture of both directly to the surface of the substrate.

Use may also be made of an atmosphere of inert gas in the case of UV curing. If a protective gas is not used, ozone may be generated. This can, for example, be extracted by suction.

Preferred radiation sources are UV emitters or electron-ray sources. UV radiation sources having emissions in the wavelength range 180 - 420 nm, and preferably 200 - 400 nm, are, for example:

optionally doped high-pressure, medium-pressure and low-pressure mercury emitters, gas discharge tubes such as low-pressure xenon lamps, pulsed and unpulsed UV lasers, UV spot-type emitters such as UV-emitting diodes. Particularly suitable radiation sources emitting in the longwave UV

spectrum are so-called black-light tubes. Measures can optionally be taken to counter the heat of the radiation source, e.g. by cooling with water or air.

Cathode-ray sources are, e.g., spot-type emitters working according to the electron-ray principle (e.g., made by Polymerphysik, Tübingen) or linear cathodes which work according to the Electrocurtain^R principle (e.g., made by Energie Science Inc). They have a radiation output of 100 keV to 1 MeV. Combinations of these radiation sources are also possible.

Both the electron sources and the UV radiation sources can also be designed to work discontinuously. Particularly suitable then are laser light sources or electron sources. Another possibility as regards the provision of UV sources capable of being rapidly switched on and off (pulsed operation) consists in the interposing of, e.g., moveable shutters.

By way of auxiliary units use may be made of conventional light-control systems which are customary in the sphere of optics technology, such as absorption filters, reflectors, mirrors, lens systems or light-wave conductors can be employed.

According to the invention irradiation can be carried out in such a way as to ensure that thorough crosslinking of the layer of clear lacquer is effected in one step. It can however also be advantageous to bring about a prior gelling of the coating film by UV-induced crosslinking, e.g. in a first zone in which black-light irradiation takes place, and then to continue crosslinking in a second step or several steps, for example by renewed UV irradiation or by irradiation with electron rays.

The arrangement of the radiation source is in principle

well-known and be adjusted to suit the conditions of the workpiece and the parameters of the process.

For example, the workpiece can be irradiated as a whole, or a radiation curtain can be used which moves in relation to the workpiece. In addition, by the use of an automatic device a spot-type radiation source can be passed over the substrate and initiate the crosslinking process. In order to achieve a crosslinking reaction on all sides of the workpiece, movement of the substrate in front of the radiation sources about the longitudinal or transverse axes is also possible.

The distance of the radiation source can be fixed or it can be adapted to a desired value according to the form of the substrate. The distances of the radiation sources from the wet-lacquer surface preferably lie in the range from 2 to 25 cm, and in particular 5 - 10 cm. If a UV laser is used, a greater distance is possible.

Of course, the process steps listed as examples can also be combined. This can be effected in a single stage of the process or in process stages temporally or spatially separated from one another.

The duration of irradiation lies for example in the range from 0.1 seconds to 30 minutes, according to lacquer system and radiation source. A duration of less than 5 minutes is preferred. The duration of irradiation is chosen in such a way as to achieve total curing, i.e. the formation of the required technological characteristics is ensured.

The process according to the invention can be used to particular advantage in the production of multi-layer lacquer coatings in the automobile industry, e.g. in the manufacture of car bodies or their parts.

A problem with the coating of automobile bodies with

radiation-curable lacquer systems lies in the cure of areas not directly accessible to radiation (shadow zones), e.g. cavities, folds and other undercuts resulting from manufacture. This problem can be solved by, e.g., using spot-type, small-area or omnidirectional emitters with an automatic movement device with a view to irradiating interiors, engine compartments, cavities or edges.

Additionally it is possible to apply a thermal activation in order to bring about crosslinking of the coating agent on surfaces which can only be inadequately subjected to the radiation-crosslinking process. When using coating agents capable of polymerisation in radicalic manner it can be advantageous in this connection to use radical initiators which can be activated thermally, so that subsequent to irradiation or simultaneously with irradiation thermally activated radicalic polymerisation can be achieved. When using cationically polymerisable coating agents it is not necessary to use special initiators which can be activated thermally. The cationic polymerisation initiated by the radiation energy also spreads to the shadow zones, e.g. the unirradiated or only slightly irradiated surfaces. It is however also advantageous in this case to apply heat in order to support polymerisation in the shadow zones.

According to the invention radiation-curable clear-lacquer coating agents can be used which are well-known in principle and described in the literature. This involves either systems which are curable in radicalic manner, i.e. by the effect of radiation on the coating agent radicals are formed which then trigger the crosslinking reaction, or systems which are curable in cationic manner, in which by irradiation of initiators Lewis acids are formed and serve to trigger the crosslinking reaction.

Systems which are curable in radicalic manner make use of, e.g., prepolymers, such as polymers or oligomers which have

olefinic double bonds in the molecule. These prepolymers can optionally be dissolved in reactive diluents, i.e. reactive liquid monomers. In addition, coating agents of this type can also contain conventional initiators, light-ray-absorbing agents and, optionally, transparent pigments, soluble dyestuffs and additional auxiliary lacquering agents.

Examples of prepolymers or oligomers are (meth)acrylic-functional (meth)acrylic copolymers, epoxide resin (meth)acrylates which are free of aromatic structural units, polyester(meth)acrylates, polyether(meth)acrylates, polyurethane(meth)acrylates, unsaturated polyesters, amino(meth)acrylates, melamine(meth)acrylates, unsaturated polyurethanes or silicon(meth)acrylates. The molecular weight (number average M_n) lies preferably in the range from 200 to 10000, and in particular from 500 to 2000. Here and in the following (meth)acrylic denotes acrylic and/or methacrylic.

If reactive diluents are employed they are generally used in quantities between 1 and 50% by weight, preferably 5 - 30% by weight, relative to the total weight of prepolymers and reactive diluents. They can be mono-, di- or polyunsaturated. Examples of such reactive diluents are: (meth)acrylic acid and its esters, maleic acid and its semi-esters, vinyl acetate, vinyl ether, substituted vinyl carbamides, alkylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, vinyl (meth)acrylate, allyl (meth)acrylate, glycerine tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, styrene, vinyl toluene, divinyl benzene, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipropylene glycol di(meth)acrylate and hexanediol di(meth)acrylate, as well as mixtures thereof. They serve to influence viscosity and technical lacquering characteristics, such as, e.g., the crosslinking density.

Photoinitiators for systems curable in radicalic manner can, e.g., be used in amounts from 0.1 to 5% by weight, preferably 0.5 - 3% by weight, relative to the total quantity of prepolymers which are polymerisable in radicalic manner, reactive diluents and initiators. It is advantageous if their absorption range is within 260 - 450 nm. Examples of photoinitiators are benzoin and derivatives, benzil and derivatives, benzophenone and derivatives, acetophenone and derivatives, e.g., 2,2-diethoxyacetophenone, thioxanthone and derivatives, anthraquinone, 1-benzoylcyclohexanol, organophosphorus compounds such as acylphosphine oxide. The photoinitiators can be used on their own or in combination. In addition, other synergistic components, e.g. tertiary amines, can be used.

In addition to the photoinitiators, conventional photosensitisers such as anthracene can also be used, if necessary, in the usual quantities, for example with a view to irradiation with black-light tubes. Additionally, radicalic initiators which can be activated thermally can optionally be used. Between 80 and 120°C these form radicals which then start the crosslinking reaction. Examples of thermolabile radicalic initiators are: organic peroxides, organic azo compounds or C-C-dissociating initiators such as dialkyl peroxides, peroxocarboxylic acids, peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azodinitriles or benzpinacolsilyl ethers. C-C-dissociating initiators are particularly preferred, since with thermal dissociation no gaseous reaction products are formed which can cause faults in the lacquer coating. The preferred quantities to be used are between 0,1 and 5% by weight relative to the total quantity of prepolymers which are polymerisable in radicalic manner, reactive diluents and initiators. The initiators can also be used in a mixture.

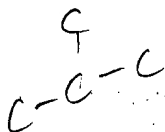
Binding agents for cationically polymerisable coating agents are for example polyfunctional epoxy oligomers which contain

more than two epoxy groups in the molecule. It is advantageous if the binding agents are free from aromatic structures. Such epoxy oligomers are, for example, described in DE-OS 36 15 790. They are, for example, polyalkylene glycol diglycidyl ethers, hydrated bisphenol-A glycidyl ethers, epoxy urethane resins, glycerine triglycidyl ethers, diglycidylhexahydrophthalate, diglycidyl esters of dimeric acids, epoxidated derivatives of (methyl)cyclohexene such as 3,4-epoxycyclohexyl-methyl-(3,4-epoxycyclohexane)carboxylate or epoxidated polybutadiene. The number average molecular weight of the polyepoxide compounds preferably lies below 10000.

If low viscosities are needed for application they can be adjusted by the use of reactive diluents, i.e. reactive liquid compounds such as cyclohexene oxide, butene oxide, butanediol diglycidyl ether or hexanediol diglycidyl ether. Examples of additional reactive solvents are alcohols, polyalkylene glycols, polyalcohols, hydroxy-functional polymers, cyclic carbonates or water. These can also contain solid constituents in solution, for example solid polyalcohols such as trimethylolpropane.

Photoinitiators for cationically curable systems are used in amounts from 0.5 to 5% by weight, on their own or in combination, relative to the total quantity of cationically polymerisable prepolymers, reactive diluents and initiators. There are substances known as onium salts which when irradiated give rise photolytically to Lewis acids. Examples are diazonium salts, sulfonium salts or iodine onium salts. Particularly preferred are triarylsulfonium salts.

Non-reactive solvents for systems which are curable in radicalic and cationic manner are conventional lacquer solvents such as esters, ethers, ketones, for example butyl acetate, ethylene glycol ether, methylethyl ketone, methylisobutylketone, as well as aromatic hydrocarbons. For



systems which are polymerisable in radicalic manner. C_2-C_4 -alkanols, and preferably water, are also suitable as solvents.

The clear lacquers used according to the invention preferably have light-ray-absorbing agents added to them. Examples of these are phenyl salicilates, benzotriazole and derivatives, HALS compounds, as well as oxalanilide derivatives, optionally also used in combination. Customary concentrations amount to 0.5 to 5% by weight, preferably 1 - 2% by weight, relative to the total quantity of clear lacquer. When choosing the light-ray-absorbing agent, attention must be given to ensuring that the initiation of crosslinking is not impaired by the light-ray-absorbing agent and that such agents that are used are stable when irradiated during the radiation-curing process.

Further additives are, for example, elastifying agents, polymerisation inhibitors, defoamers, levelling agents, anti-oxidation agents, transparent dyestuffs or optical brightening agents.

Transparent colourless fillers and/or pigments can optionally be added to the coating agent. The amount used is up to 10% by weight, relative to the total amount of clear lacquer. Examples are silicon dioxide, mica, magnesium oxide, titanium dioxide or barium sulphate. The size of the particles preferably lies below 200 nm. With UV-curable systems attention should be given to ensuring that the coating film in the layer thickness used remains transparent to UV radiation. Additional useable additives are, for example, conventional inorganic or organic delustering agents. These can be added in conventional amounts, for example up to 10% by weight. Examples of delustering agents are silicates, pyrogenic silicic acids such as aerosil, bentone or condensed and crosslinked urea formaldehyde resins, natural and synthetic waxes. The particle sizes of such delustering

agents lie generally in a range up to 100 μm , and preferably up to 30 μm .

The stages of the process for producing suitable radiation-curable clear-lacquer coating agents are well-known. It is possible to combine systems with different radiation-induced chemical crosslinking mechanisms. These can be various crosslinking systems curable in radicalic manner, or cationically curable crosslinking systems, or radically and cationically curable crosslinking combined with one another. Attention should be given to choosing the composition in such a way as to ensure long storage life. Likewise different reaction-initiating processes can be combined, for example UV with UV curing, UV with thermal initiation or electron-ray curing with UV curing.

The various crosslinking reactions can be started with mixtures of suitable initiators. For example, mixtures of UV initiators with differing maximum absorption characteristics are possible. In this way various emission maxima of one or several radiation sources can be utilised. This can be effected simultaneously or in sequence. For example, curing can be initiated with radiation from one radiation source and continued with that from another. The reaction can then be carried out in two or more stages, optionally also separated spatially. The radiation sources used can be the same or different.

According to the invention it is possible to carry out firstly a radiation-induced and then or simultaneously a thermally induced crosslinking reaction. To this end, in addition to one or several photoinitiators, one or several thermally dissociating initiators can optionally be used. The use of photoinitiators is not necessary when curing by electron rays.

Two- or multi-stage operation can be advantageous, in order,

for example, to achieve initial gelling, whereby for example runs on lacquered vertical surfaces can be avoided. Gelling is also advantageous in the case of solvent-based systems, in order to allow evaporation of the solvent.

The photoinitiators are preferably chosen in such a way that they do not decay in light having a wavelength of over 550 nm. With the use of thermally dissociating initiators these should be chosen in such a way as to ensure that they do not decay under the conditions of application of the lacquer material. In this way it is possible to recycle the overspray of the coating agent directly and to re-use it, since a chemical reaction is avoided during application.

The crosslinking density of the lacquer films can be adjusted by the functionality of the components of the binding agent employed. The choice can be made in such a way as to ensure that the crosslinked clear-lacquer coating has sufficient hardness and that too high a degree of crosslinking is avoided, in order to prevent the film from becoming too brittle.

By means of the process according to the invention multi-layer coatings are obtained which constitute a clear-lacquer surface with high resistance to scratching and also a high degree of gloss, as well as a high degree of mechanical durability. As a result of the process parameters and the chosen crosslinking mechanism, at the same time the overspray of the coating agent to be applied can be made available for immediate re-use. The process according to the invention is particularly suitable for use in series production lacquering in the automobile industry; for example, for the lacquering of car bodies and their parts.

In all the examples described below, application of the radiation-curable clear lacquers was performed in a room illuminated exclusively by red-light sources (light

wavelength greater than 600 nm).

Example 1

By mixing the following components a radiation-curable clear-lacquer coating agent was formed:

% by weight

44.5	Novacure 3200	(aliphatic epoxy acrylate made by Interorgane)
32.2	Ebecryl 264	(aliphatic urethane acrylate made by UCB)
3.0	Irgacure 184	(photoinitiator made by CIBA)
10.0	dipropylene glycol diacrylate	
10.0	trimethylolpropane triacrylate	
0.3	Ebecryl 350	(silicon acrylate made by UCB)

OK gm

Subsequently a lacquer structure was produced as follows:

A metal plate with a primer composed of KTL (20 μ m) and pre-coated with filler which is customary in the trade (35 μ m) was coated in one case with conventional water-based lacquer, in a second case with solvent-containing basecoat (15 μ m dry layer thickness), and then in both cases stoved for 20 min at 140°C. Subsequently the above lacquer system was applied with a layer thickness of 35 μ m.

Given a belt velocity of 9 m/min, curing of the horizontal metal test plate was effected by irradiation by two medium-pressure mercury emitters, each of which having an output of 100 W/cm and placed at a distance of 10 cm from the surface to be cured (duration of irradiation 1 - 2 sec). A shiny and hard surface with good adhesion was obtained on both the aqueous basecoat and the conventional basecoat.

Example 2

% by weight

40.5 Novacure 3200

27.5 Ebecryl 264

2.0 C-C-dissociating initiator (tetraphenylethane
derivative according to
DE-A-1 219 224)

2.0 Irgacure 184

10.0 dipropylene glycol diacrylate

10.0 tripropylene glycol diacrylate

0.3 Ebecryl 350

7.7 vinyl toluene

A metal test plate was produced in a similar way to that described in Example 1, in this case however coated on both sides, and after application of the above radiation-curable clear lacquer it was irradiated on just one side while freely suspended, the side to be irradiated being moved evenly, at a distance of 10 cm and within 5 sec, past a medium-pressure mercury emitter as stated in Example 1.

The tacky rear side which was only partially crosslinked by irradiation was stoved for 15 min at 110°C in an air-circulating furnace.

Surfaces were obtained on both sides of the metal test plate with characteristics as described in Example 1.

Example 3

(radiation-induced cationically curable clear lacquer)

% by weight

60.0 Degacure K 126 (cycloaliphatic epoxide made by
DEGUSSA)

25.0 Araldit DY 026 (hexanediol diglycidyl ether made by
CIBA)

- 4.5 Degacure 85 (sulfonium salt made by DSSA)
0.5 Dynasilan Glymo (glycidyl-functional silane made by
Dynamit Nobel)
10.0 cyclohexanol

With this formulation the procedure was completely analogous to that in Example 1. A similar lacquer was obtained.

Example 4

Example 1 was repeated, with the same lacquer result. The only difference being that the basecoat layers here were stoved for 30 min at 120°C and pre-coated polycarbonate sheets were used.

Example 5

To 100 parts of the clear-lacquer coating agent from Example 1, two parts of anthracene were added as photosensitiser. Application was effected as described in Example 1. Then irradiation was effected at a belt velocity of 1 m/min, lying flat, with 10 black-light tubes at a distance of 10 cm from the wet-lacquer surface (duration of irradiation 90 - 120 sec). A tacky, partially crosslinked surface was obtained. Then the metal test plate was suspended for 5 min and then, hanging free, irradiated, the still tacky surface being moved uniformly, at a distance of 10 cm and within 5 sec, past a medium-pressure mercury emitter as stated in Example 1. A lacquer result as stated in Example 1 was obtained. The surface was free from runs.